Correlation of chemical composition and odor concentration for emissions from pig slaughterhouse sludge composting and storage

Vincent Blazy, Amaury De-Guardia, Jean Claude Benoist, Mylène Daumoin, Fabrice Guiziou, Marguerite Lemasle, Dominique Wolbert, Suzelle Barrington

Correlation of chemical composition and odor concentration for emissions from pig slaughterhouse sludge composting and storage

V. Blazy*[A], A. De-Guardia[A], J.C Benoist[A], M. Daumoin[A], F. Guiziou[A], M. Lemasle[B], D.Wolbert[B], S. Barrington[A,C],

[A] *Irstea, UR GERE, 17 Avenue de Cucillé, CS 64427, F-35044 Rennes, France.*

[B] *Laboratoire Sciences Chimiques de Rennes - équipe Chimie et Ingénierie des Procédés, UMR 6226 CNRS, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France.*

[C] *Concordia University, Department of Building, Civil and Environmental Engineering, 1455 de Maisonneuve, Montréal, QC H3G 1M8, Canada.*[1]

*Corresponding author: Phone: +33 2 99 29 91 57; fax: +33 2 23 48 21 15.

E-mail address: vincent.blazy@irstea.fr (V. Blazy)*, amaury.de-guardia@irstea.fr (A. De-Guardia), jean-claude.benoist@irstea.fr (J.C. Benoist), mylene.daumoin@irstea.fr (M. Daumoin, France), fabrice.guiziou@irstea.fr (F. Guiziou), marguerite.lemasle@ensc-rennes.fr (M. Lemasle), dominique.wolbert@ensc-rennes.fr (D.Wolbert), suzellebarrington@sympatico.ca (S. Barrington).

Abbreviations :
BA, bulking agent ; CH_3SH, methanethiol ; GC-MS, gas chromatograph coupled with a mass spectrometer ; H_2S, hydrogen sulfide; MDL, sampling and GC-MS method detection limit; NH_3, ammonia ; OAV, odor activity value of a gaseous odorous compound defined as the ratio of its concentration to its odor detection threshold; OC, odor concentration of a gas volume measured by olfactometry and corresponding to the number of dilution required in order its odor is not detected anymore ; OC_{INT}, bound of the confidence interval of the odor concentration measure, OAV_{MAX}, odor activity value of the compound exhibiting the highest concentration to ODT ratio in a gaseous mixture; OAV_{MAX2}: odor activity value of the compound exhibiting the second highest concentration to ODT ratio in a gaseous mixture; OAV_{SUM}, summation of the odor activity values of every odorous compound contained in a gaseous mixture ; ODT, odor detection threshold ; PSS, pig slaughterhouse sludge ; RSH, mercaptan ; TMA, trimethylamine ; RD, Relative Deviation ; VOC, volatile organic compound.

Abstract

The objective of this study was to correlate the chemical composition and the odor concentration of emissions produced during storage and composting of pig slaughterhouse sludge (PSS). Seven experimental conditions were monitored using composting reactors with forced aeration and cells designed to simulate storage. Sixty six gas samples were collected and characterized by both GC-MS and olfactometry. Two types of correlation were investigated between the chemical composition and the odor concentration (OC) of every gas sample. The odor activity value for a given emitted compound (OAV) was computed as the ratio of its chemical concentration to its odor detection threshold (ODT). The correlation OAV_{MAX} considered that the OC of a gas sample was equal to its highest OAV whereas the correlation OAV_{SUM} considered that the odor of the gas sample was equal to the sum of the OAV of every compound contained in the gas sample. As per Standard EN 13725, both OAV_{MAX} and OAV_{SUM} were compared using a confidence level for OC defined as [OC/1.65 to 1.65 x OC]. Whereas OAV_{MAX} values were within the confidence level of OC for 62% of the 66 gas samples, OAV_{SUM} values were within this confidence level for only 53%. Validating OAV_{MAX} as a satisfying correlation between chemical composition and OC, only three compounds among the 66 identified namely trimethylamine, hydrogen sulfide and methanethiol, accounted for the prediction of OC measured during composting and storage of PSS.

Highlights

PSS composting and storage gas samples were determined by chemical and olfactory analyses

For gas samples, correlations between the chemical composition and its OC was investigated

OAV_{MAX} assumed that OC was equal to the sample's highest OAV value

OAV_{SUM} assumed that OC was equal to the sum of all OAV for sample

The 3 most odorant compound offered a good prediction of the olfactory results.

Keywords: gaseous emission, odor, chemical composition, composting, storage, pig slaughter house sludge

1. Introduction

Odor emissions from composting plants are a common source of annoyance. Odorous nuisance can have significant impact on environmental health [1] and the quality of life. Negative neighbourhood reactions to composting odors may lead to temporary or definite closure and a lack of acceptance of new facilities [2]. Good management of composting operations can help minimize odor impacts, although odor generation cannot be avoided [3]. Odor management should take into account operational conditions such as composting facility aeration process, levels of confinement, emission sources identification, collecting and treatment of gaseous emissions [4]. Such difficulties in controlling compost facility odor nuisance demonstrate the lack of efficiency of present and often expensive solution technologies.

Cost-effective strategies for solving odor problems require the identification of the major contributing odorants compounds as found in the gaseous mixture released [5]. This requires the correlation of the emission's chemical composition and its odor concentration. Targeting the most responsible compounds, such correlation can provide criteria for the development of: i) odor prevention and abatement strategies; ii) odor characterization using analysis of specific indicator compounds, and; iii) specific sensors for online odor monitoring.

The first main step towards linking the chemical composition of a sample and its odor concentration is to define how to integrate the odorous potential of an individual compound in a complex odor mixture. Indeed, each compound contributes to a different extent to overall odor concentration [6]. Based on the odor detection threshold (ODT-the minimal concentration of a single compound which is perceived by 50% of the population), the odor activity value (OAV) has been widely used [6-11]. It was defined as the ratio of the chemical concentration to the odor detection threshold of a single targeted compound within a sample. The odor activity value is a dimensionless value also interpreted as the theoretical dilution factor required to reach the odor detection threshold of the compound. Thus, the first step in achieving this correlation consists in linking the odor activity value of individual compound (or their theoretical dilutions factors) to the dilution factor required by olfactometry to reach the threshold dilution for the complex emission. This dilution factor is equivalent to its odor concentration, or OC, as defined by EN 13 725 [12]. A first mathematical function used to correlate the odor activity value (OAV) and the odor concentration (OC) consisted in numerically adding the OAV of all individual compound identified in the emission (OAV_{SUM}). The value OAV_{SUM} was used by Gallego et al. [11] to

predict the concentration of composting odors in the absence of olfactometry. For odorous emissions produced by food and industrial wastes, Kim and Park [9] found a strong correlation between OC and OAV_{SUM}. In contrast, for odor emissions from cattle shelters, Parker et al. [6] found a poor correlation (R^2= 0.16 to 0.52) between OC and OAV_{SUM}.

Taking into account potential synergic effects between a large numbers of compounds, multivariate analyses coupled with regression methods were widely investigated. These complex methods were directly used by: Noble et al. [13] for mushroom composting; Hanajima et al. [14] for swine manure; Mao et al. [15] and Tsai et al. [2] for food waste, and; Defoer et al. [16] for green waste. Multivariate analyses were also used to correlate odor to odorant compounds for swine facilities [17-18] or the headspace above stored slurry [19-20]. These investigations produced no clear correlation allowing for the prediction of composting or livestock odor. Indeed, each model led to a specific relationship [16] and moreover, showed no cause-and-effect relationship [5] between the odor concentration and the chemical composition of the gaseous samples. These drawbacks indicated the complexity of the human sensory perception and the limits of these methods.

The objective of this study was to find a simpler and generic model to correlate the chemical composition and the odor concentration of emissions produced during composting under forced aeration and during storage. Pig slaughterhouse sludge (PSS) was the waste studied in this experiment. Seven laboratory experiments were monitored to simulate composting and storage of PSS. Sixty six gas samples were collected and characterized by both GC-MS and olfactometry. Two types of correlation were investigated to link the chemical composition and the odor concentration (OC) of every gas sample: the first was the sum of the odor activity values (OAV_{SUM}), defined earlier, and; the second was

OAV_{MAX} consisting of the highest OAV value associated with an individual compound within the sample.

2. Materials and methods

2.1. Experimental conditions

The composting experiments were performed in 300 L reactors consisting of insulated stainless cylinders, 800 mm in height and 700 mm in diameter. Immediately after loading the reactors, a low aeration rate of 1.3 $L.h^{-1}.kg^{-1}$ of wet sludge was applied during 5 days. Thereafter, the aeration rate was increased to 9.3 $L.h^{-1}.kg^{-1}$ wet sludge and maintained constant till the end of the experiment. A rotameter (FL-821-V, OMEGA Engineering Inc., Stamford, USA) regulated the in-coming airflow while a volumetric gas meter measured the flow (Gallus 2000,Actaris, Liberty Lake, USA). The reactor were equipped to continuously monitor the compost temperature and its total mass using respectively two Pt100 probes and weigh sensors. Concentrations in O_2 and CO_2 were continuously measured in both the in-coming and out-going airflows using respectively a paramagnetic analyzer (MAGNOS 206, ABB, Zurich, Switzerland) and an IR spectrometric analyzer (URAS 26, ABB, Zurich, Switzerland). Every 10 days, the compost was turned. The composting treatment was stopped after 36 days.

The composting experiments were carried out using PSS mixed with bulking agent. The sludge was collected from the primary wastewater treatment process of a pig slaughterhouse. The primary pig slaughterhouse sludge had collected at the plant, following

its sieving using 6 mm and 1 mm sieves, its coagulation and flotation, and its centrifugation. At the laboratory, the sludge was stored in bags at -18°C. The content of each bag was dumped into opened bins to be thawed at 4°C, one week before being used.

The bulking agent (BA) consisted of oak and ekki wood chips with a particle size ranging from 0 to 40 mm. The characteristics of the feedstock (pig slaughterhouse sludge plus wood chips) are provided in the supplementary materials 1. The wet mass BA/PSS ratios applied were respectively 0.55 and 0.73 $kg.kg^{-1}$. For a BA/PSS of 0.73 $kg.kg^{-1}$, the two moisture contents tested were 61.2 % to 63.7 %.

The storage cells were 28 L airtight stainless steel cylindrical vessels, with a height of 900 mm height and a diameter of 200 mm. The cover of the storage vessel was equipped with an air inlet and outlet to sample the volume over the stored material. Each vessel was filled with 720 mm of PSS with and without BA. A constant aeration rate of 40 $L.h^{-1}$ was applied to the cell, for a value of 1.72 to 3.95 $L.h^{-1}.kg^{-1}$ of wet material. The gas samples were collected by connecting bags to the storage vessel ventilation exhaust port. The vessels were emptied after 14 to 30 days of storage.

The storage vessels were filled with fresh PSS, fresh PSS mixed with BA, and PSS composted for 15 and 30 days. The PSS composts were obtained from the composting experiments carried out with a BA/PSS ratio of 0.83 $kg.kg^{-1}$ and under an aeration rate of 6.05 $L.h^{-1}.kg^{-1}$ of wet sludge. For the storage experiments with PSS composts, the larger wood chip particles were removed from the PSS + BA composted mixture using a rotary sieve with 10 mm openings.

156 **Table 1**

157 Mixtures compositions and experimental conditions

158

159 2.2. Gas sampling, pre-dilution and preparation before odor measurement

160 The samples were collected manually using single-use Nalophan bags (EN 13 725
161 [12]), with a volume of 35 to 70 L, depending on the expected odor concentration.
162 Nalophan bags were directly connected to the reactor exhaust or to the storage vessel
163 sampling port. It took from 30 to 60 minutes to fill the Nalophan bags depending on their
164 volume and the treatment aeration rate. A glass bottle condenser was placed between the
165 reactor exhaust and the bag used for sampling, to remove condensate, during the initial
166 period of composting when hot moist gases were released. Gaseous emissions were
167 sampled every two days from the start, still the end of each experiment. For each sampling
168 session, two to three Nalophan bags were filled to duplicate or triplicate the measurement
169 results. The analysis of several samples at any given time enhanced the accuracy of the
170 odor concentration measurements.

171 To limit deterioration, chemical composition and odor concentrations measurements
172 were conducted within 4 to 6 hours of collection. When possible, both analyses were
173 carried out in less than few hours. The removal of water before sampling and the use of
174 sampling bags could lead to odorant losses [8, 21], and consequently odor emission
175 underestimation. It has been demonstrated that sample odor decreased when stored over 24
176 hours. Indeed, the recovery of odorants stored in sampling Tedlar bags [22-23-24], or
177 Tedlar versus Nalophan [25-26-27] was analyzed after 4 to 24hours, to show that most
178 odorants can be lost after 24 hours [12]. Less than 5 and 10% of the odor of methanethiol,

dimethyl sulfide and hydrogen sulfide was lost respectively in Tedlar and Nalophan bags, after 4 to 8 hours of storage [25-26-27]. Even though the recovery of odorants in sampling bags is an important issue and can lead to odor concentration underestimation, Van Harreveld [28] showed that odor is stable in Nalophan bags for a period of 4 to 12 hours. Since sample bags were analyzed within 4 to 6 hours and because of similar treatment, chemical composition and odor concentration from the same sampling bag could be compared and considered to represent the emission sampled.

Since gaseous emissions from the raw compost required a large dilution level before olfactometry, namely 131,000 folds, samples had to be pre-diluted, using three methods providing a range of 12.6 to 500. The first method consisted in directly connecting to the olfactometer, a double orifice probe mixing the gas sample with dry clean air, where the size of the respective orifices provided a dilution ratio of 100. The dilution rate of the probe was controlled using a Gilibrator 2 calibration system (Gilian, Clearwater, USA). The second method consisted in precisely measuring 250 mL of gas sample using a glass sampling bulb with a PTFE stopcock (Supelco, Bellefonte,USA). Using the olfactometer, the 250 ml volume was then injected into a Nalophan bag containing 5, 30 or 35L of dry clean air for a dilution rate of respectively of 21, 121 or 141. Thus, the accuracy of the dilution was determined by that of the olfactometer airflow controls. The third dilution method consisted in withdrawing a diluted sample from a Nalophan bag using a gas tight syringe (Supelco) and then injecting into a new Nalophan bag filled with a known volume of clean air. The pre-diluted rate was applied to the odor concentration level measured by olfactometry. According to Wardencki [29], the collection and storage of gas samples in a glass bulb leads to a significant loss of hydrogen sulfide and methanethiol. However, in this

study, glass bulbs or glass syringes were sparsely used even to stored samples for less than few minutes before being mixed with dry and odorless gas in Nalophan bags. Moreover, as described below for the composting experiments, a glass condenser preceded the hydrogen sulfide and mercaptan traps. Because a similar treatment was used for all samples, hydrogen sulfide and mercaptan odor concentration could be compared.

When possible, a pure and a pre-diluted bag were analyzed to verify the dilution accuracy and adjust the dilution coefficient for olfactometric characterization. This coefficient was computed by dividing the carbon mass from each compound of the two bags. Pre-dilution factor ranged from 3 % to 39 % with a mean value of 19.5 %, and the use of a correction factor improved the accuracy of the pre-dilution procedure. However, the relative OC deviation measured between two pre-diluted bags from the same sample ranged from 0 to 20.8% with a mean value of 10.3% against 9.8% for the bags analyzed without pre-dilution. This low difference showed that even though the accuracy of the pre-dilution methods had to be corrected, their repeatability was quite satisfactory (data not shown). In decreasing order, the accuracy of the dilution methods are: gas tight syringe; glass sampling bulb, and; dilution probes. Since many samplings required a dilution factor of over 100, the glass sampling bulb was mostly used. The tight syringe was used only once for each composting reactors, just before the composting airflow adjustment because of the low aeration rate resulting in highly concentrated samples required a dilutions factor of 200 to 500.

2.3. Olfactory measurements

The dynamic dilution olfactometer ONOSE-8 (Consumaj, Canada) was used to determine the odor concentrations (OC) of the studied samples. The Onose-8 olfactometer was designed to respect the EN 13725 [12] standards. The apparatus was calibrated using the Gilibrator 2 calibration system (Gilian, Clearwater, USA) which handles a wide range of flow rates.

The olfactory method consisted in firstly applying a dilution rate to the gas sample high enough not to be detected by the 6 panellists. Then, the dilution rate was reduced until odor was detected. The mass flow controllers of the ONOSE-8 provide a dilution scale ranging from 16 to 131 000. Triple force-choice was the principle used where all trained panelists have to identify among three ports that contaminated. The panelist group consisted of 19 persons, each being selected based on their sensitivity to the n-butanol reference gas as described in the EN 13725 [12] standards. At least 6 odor panelists were selected for each olfactometric session. Each bag, even from identical sampling, was presented three times to the panel. The first presentation used a dilution step factor of 4, to rapidly introduce the panelists to the odor stimuli. The result of this presentation was systematically removed and not considered. Then, two additional series of ascending concentration ratios with a step factor of 2 were presented to prevent olfactory adaptation or a loss of sensitivity. The geometric mean of the panel detection thresholds from these two series was used to compute the odor concentration of the sub-sample contained in the bag. The final odor concentration of the gas sample, expressed in $OU.m^{-3}$, was the geometric mean of the odor concentrations of the 2 to 3 bags analyzed. All the odor concentrations of each sample analyzed are shown in the supplementary material 2. According to Hansen et al., [30-31], olfactometer dilution systems can alter the odorous charge of a compound. Reduced sulfure

247 compounds, such as hydrogen sulfide, methanethiol and dimethyl sulfide, can be affected
248 differently when flowing through the olfactometer system, as they can suffer an average
249 loss of 55-60%, 27-35% and 9.3-21%, respectively. Furthermore, the recovery of other
250 odorants, such as carboxylic acids, trimethylamine and 3-methylphenol, were also
251 significantly affected by the pulse duration leading to unstable signals within the 60-second
252 pulse. Although such losses were not investigated in this study, the Onose-8 olfactometer
253 offers accurate mass flow controllers with a limited error margin of ±0.2% (0% to 20% of
254 the total range) and ±1% (20% to 100% of the total range). Moreover, panelists were
255 invited to detect the odorous stimulus after the mass flow controllers showed a stable
256 signal. This precaution favors odorant recovery.
257
258 2.4. Chemical characterization of gases
259
260 *2.4.1. Quantification of NH_3, H_2S and mercaptans emissions*
261 Using airflow taps on the gas exhaust lines after the glass condenser, two gas lines
262 were placed in parallel: the first to trap ammonia (NH_3) in sulfuric acid (H_2SO_4, 1N), and;
263 the second to trap in series, hydrogen sulfide (H_2S) in a formic/formate acid buffer solution
264 0.1N with 10 $mg.L^{-1}$ lead nitrate ($PbNO_3$), and then mercaptans (RSH) in acid (0.1 N) with
265 10 $mg.L^{-1}$ mercuric dichloride ($HgCl_2$). The aeration rate through each line, namely for the
266 NH_3 and H_2S traps, followed in series by the RSH trap, was fixed by a flow meter (FL-821-
267 V, OMEGA Engineering Inc., USA) at 80 $L.h^{-1}$ and measured using a volumetric gas meter
268 (Gallus 2000, USA).

For the NH_3 traps, NH_4^+/NH_3 content was quantified by steam distillation (method modified from NFT 90-015-1 [32], Gerhardt Vapodest 50, Germany) into boric acid (H_3BO_3, 40 $g.L^{-1}$) and then back-titration with sulfuric acid (H_2SO_4, 0.2 N). Duplicate results were validated by a coefficient of variation below 5%. The titration detection limit was 0.014 $mgN.mL^{-1}$ of trap. Considering the mean trap volume of 200mL at a density of 1023 $g.m^{-3}$ during a sampling period of 24h, the method detection limits for ammonia in the exhaust gas was 0.286 $mg.m^{-3}$. The reaction of H_2S with $PbNO_3$ and of RSH with $HgCl_2$ produced a PbS and $Hg(SR)_2$ precipitate recovered by filtration through glass fibre filters (Satorius, France). The precipitates were dried at 55°C and weighed. In this study, all mercaptans emissions trapped in $HgCl_2$ were calculated as methanethiol leading to $Hg(SCH_3)_2$ precipitate. This potentially led to under-estimating the odor contribution of mercaptans since the odor detection threshold of methanethiol is higher than that of other mercaptans such as ethanethiol, propanethiol, and 1- butanethiol. The concentrations of the compounds analysed by chemical traps was computed as the mean values of their emissions between two odor sampling sessions.

For the composting experiments, the traps were changed every 24h for the first 15 days and then every time the gas was sampled for odor measurement. For the storage experiments, the traps were also changed every time the gas was sampled for odor measurement, namely every two days. Saturation was never observed for the NH_3, H_2S and RSH traps.

290 *2.4.2. VOCs identification and quantification*

291 The chemical gas samples characterization included the identification and the
292 quantification of VOCs. Thus, the gas samples collected in Nalophan bags were
293 concentrated by passing through Carbotraps (Carbotrap 349, PerkinElmer, USA) using a
294 vacuum pump (Giliar, USA) equipped with a constant low flow module set at 50 $mL.min^{-1}$.
295 Considering that VOCs concentrations were unknown, several Carbotraps were prepared
296 for each sample by passing different volumes, namely 500, 1000, 1500, 3000 mL.
297 Accordingly, such volumes were associated with detection limits of 80, 40, 26 and 13
298 $\mu g.m^{-3}$, respectively. The Carbotraps were stored at 4°C for less than one week before
299 being desorbed and analyzed by GC-MS [33].

300 The desorption was carried out by a Thermal Desorption unit (TurboMatrix 550,
301 Perkin Elmer) coupled with a Clarus 500 GC-MS detector (Perkin Elmer). Then, these were
302 separated through the capillary column (CP-WAX 58, 25m x 0.15mm; Film 0.25 Varian,
303 USA). Analytical conditions of thermal desorption and column separation, were provided
304 by Blazy et al. [34]. Chromatogram processing depended on the detection mode used by
305 mass spectrometry for detecting separated compounds. Indeed, 2 simultaneous acquiring
306 modes were used. A full scan (FS) acquisition (20-300 amu) allowed for the identification
307 of compounds with 2 sets of criteria: (1) GC retention times and mass spectra matched with
308 the calibrated compounds, and; (2) the mass spectra obtained from a reference library
309 (National Institute of Standards and Technology, NIST, Gaithersburg, USA). A quantitative
310 assessment of VOCs was performed by a single ion resolution (SIR) acquisition which
311 quantified specific masses of compounds (m/z, major characteristic ion in the spectra) as

area counts under peaks for separated VOCs. A calibration was performed to convert the measured area into a compound mass.

The calibration procedure consisted in injecting into an N_2 filled Tedlar bags, a known volume of the compound of high purity (Acros Organics, Alfa Aesar or Sigma Aldrich) at a concentrations of 13 to 5000 $\mu g.m^{-3}$. According to the method described previously, each bagged compound was trapped onto a Carbotrap and thereafter analyzed by GC-MS. The fact that the Tedlar bags could not recovery the total amount of injected compound lead to an underestimation of the GC-MS quantification. Finally, the calibration curves were obtained by plotting the GC integrated areas versus the concentration of the bagged compound. A linear regression curve was obtained with the calibration data, except with light amines at low concentrations because of their poor detection by GC-MS, as expected. This process also demonstrated that the thermal desorption allowed to recover a very high percentage of the trapped VOCs.

The GC-MS was not calibrated for all identified compound. Non calibrated compounds were quantified by assuming a response factor equal to 1000, which represents the average value obtained with all of the calibrations.

3. Results and discussion

3.1. Determination and evaluation of odor activity

The GC-MS analysis of the 66 samples yielded 39 compounds presented in the Table 2 along with: their CAS (Chemical Abstracts Service) number; the ion used for their quantification; whether or not they associated with a calibration procedure and; their odor

335 detection thresholds (ODT) as per a recent database [36]. When several odor detection
336 thresholds were available for a single compound, only the most recent value was used. In
337 general, recent odor detection threshold values were lower than the old ones, leading to
338 higher odor activity values. However, the order of magnitude for many individual
339 compounds could be considerably different [6-11]. According to Parker et al [6], the
340 central tendency of the odor detection threshold values was well descript by geometric
341 means compared to harmonic means (which were lower) and arithmetic means (which were
342 higher and influenced by the larger individual values). Thus when several recent odor
343 detection threshold values were available, a geometric mean was used in order to obtain a
344 central tendency of the odor activity value.

345 As highlighted for some compounds in Table 2, the GC-MS detection level (method
346 detection limit or MDL) was higher than the odor detection threshold, leading for some
347 samples, to the under-estimation of the odor activity value. In Table 2, the ratio
348 (MDL_{MAX})/ODT indicates the level of underestimation for these compounds, where
349 MDL_{MAX} is the highest method detection limits observed during samples according the gas
350 volume passed throughout Carbotraps. Nevertheless, only trimethylamine (TMA) showed
351 an important odor activity value underestimation, with an MDL_{MIN}/ODT and
352 MDL_{MAX}/ODT ranging between 217 and l1333, respectively. Sulfurs, aldehyde and alcohol
353 compounds showed a maximal OAV underestimation of around 10, or even less. For such
354 compounds, the method detection limits showed low underestimation of odor activity value
355 determination.

356

357 **Table 2**

Gaseous compounds identified from emissions collected during the composting and the storage of pig slaughterhouse sludge

A last and important bias for odor activity value determination can result from the use of sorbent tubes and the subsequent thermal desorption in TD-GC/MS. Indeed, mercaptans and especially methanethiol can be oxidized to form di- and tri-sulfides [59] which were largely quantified during chromatogram processing. This reinforces the assumption that mercaptan were mainly methanethiol. Consequently, the odor activity value from methanethiol could double when adding the odor activity value from organo-sulfides, thus leading to odor activity values overestimation. However, the source of the organo-sulfide was uncertain, whether from composting or from mercaptan oxidization, or from a combination of both.

For every compound, its odor activity value (OAV) was calculated from the ratio of its chemical concentration to its odor detection threshold. All the chemical concentrations and OAV are provided in Supplementary Materials 3 and 4, respectively. The odor activity values of methenamine, 1,3 pentadiene and 3-pentanone-2-methyl were not calculated because of their unknown odor detection threshold.

Two correlations were calculated to link gas sample odor concentration (OC) to its chemical composition: OAV_{MAX}, assuming that odor concentration is equal to the OAV of the most odorous compound, and; OAV_{SUM}, assuming that odor concentration is equal to the sum of all compound OAV. The values of OC, and OAV_{MAX} and $OAV_{MAX\,2}$ (the first and second highest odor activity value per sample) and OAV_{SUM} are given in Supplementary Material 4.

The relevance of the two types of correlation was evaluated based on the percentage by which OAV_{MAX} and OAV_{SUM} fell within the 95% interval of confidence for the corresponding measured odor concentration (OC), as computed for every sample (EN 13725 [12]):

$$OC / (10^{2.0} * Sr / \sqrt{n}) < OC < OC * (10^{2.0} * Sr / \sqrt{n})$$

with, n is the number of bags analyzed, from 1 to 3, and Sr is the standard deviation calculated from the repeatability, namely 0.1721. The mean value of $(10^{2.0} * Sr / \sqrt{n})$ was found to be 1.65, whereby OC / 1.65 < OC < OC x 1.65.

Consequently, each odor concentration (OC) measure is linked to: two boundaries of the confidence interval as above-mentioned, the highest odor activity value (OAV_{MAX}) (resulting from a single compound) and the sum of the odor activity values from all compounds in the gas sample (OAV_{SUM}).

The correlation extent between OC and either OAV_{MAX} or OAV_{SUM} was estimated through a simple linear regression using a log transformation to limit distribution variance between the variables (OAV_{SUM}, OAV_{MAX} and OC). This log transformation better illustrated data patterns and allowed for the use of a simple correlation type $Log(OAV_{MAX})$ or $Log(OAV_{SUM}) = 1\ Log(OC)$ to link the variables. The logarithmic expression of the odor concentration should not be considered as an indirect indicator of the odor intensity, and extension of odor concentration. Moreover, using a "log-log correlation" graphically favors a closeness between OC and OAV_{MAX} or OAV_{SUM}, especially for high values of OC.

Therefore, the relevance of OAV_{SUM} and OAV_{MAX} predictions were also estimated on the basis of the Relative Deviation, computed for the mixtures showing an OAV_{MAX} or

OAV_{SUM} prediction outside the confidence interval of odor concentrations. Values for Relative Deviations (RDs) were computed with the closest odor concentration interval bounds (OC_{INT}) according to the Eq.1:

$$RD= (|OAV_{MAX} \text{ or } OAV_{SUM}-OC_{INT}|)*100/ OC_{INT} \quad (1)$$

with OC_{INT} being the closest interval bounds of OAV_{MAX} or OAV_{SUM}, in $OU.m^{-3}$, and where OAV_{MAX} and OAV_{SUM} are dimensionless. Values for Relative Deviation (RD) are found in Supplementary Material 5 and expressed in %. A box plot figure was drawn to study the distributional characteristics of the RD of OAV_{MAX} and OAV_{SUM} predictions with OC_{INT}.

Only the sum of the odor activity values (OAV_{SUM}) determination was affected by underestimation resulting from method detection limit. Therefore, the influence of the method detection limits on OAV_{SUM} computations was investigated. The maximum underestimated odor activity value is computed (supplementary material 4), defined as the ratio between the method detection limits by the odor detection threshold of the compounds, and added in the OAV_{SUM} computation. The method detection limits was observed to produce 0 to 55% deviation on the sum of the odor activity values (supplementary material 4). Trimethylamine has a very low odor detection threshold mainly involved in the determination of OAV_{SUM}. However, the mean Relative Deviation between the computed OAV_{SUM} (with or without taking in account the method detection limit) was of 5.6%, indicating a limited influence of method detection limits on OAV_{SUM} determination.

3.2. Qualitative evaluation of the highest odor activity value and the sum of the odor activity value from a gas sample

Olfactometry consists initially in diluting a gas sample until its odor cannot be perceived by all panellists, and then, increasing its concentration, with lower dilutions, until all trained human panelists are able to detect the odor. Theoretically in the absence of synergistic effects, the olfactory stimulus should come from the most odorant compound namely the one requiring the highest dilution rate to be odorless. In this context, Zahn et al. [60] showed that the synergistic effects were minor for swine odors. Thus, odor concentration should correlate to the odor activity value of the most odorant compound namely OAV_{MAX}. Considering the 66 gas samples analyzed, OAV_{MAX} displayed only three compounds responsible for the odors, namely mercaptans (presumed to be methanethiol), trimethylamine and hydrogen sulfide, respectively at 64, 21 and 15% of the gaseous mixtures studied. Similarly by multivariate analyses, Hansen et al. [18] identified hydrogen sulfide, methanethiol, trimethylamine, and 4-methylphenol as the main odorous compounds emitted from growing-finishing hogs facilities. Finally, these three compounds were presumed to be mostly responsible for odor concentration (OC) because of their very high odor activity values (OAV) in all 66 samples.

Fig. 1 gives Log (OAV_{MAX}) values as function of Log (OC). The dotted lines represent the 95 % confidence interval for Log (OC), namely Log (OC / 1.65) < Log (OC) < Log (OC * 1.65). The values for Log (OAV_{MAX}) fell outside this interval mostly for mixtures within methanethiol, estimated as the most odorous compound and especially at low and high concentrations, namely when OAV_{MAX} was under 8×10^3 and over 6×10^4. This resulted either from the low relevance of the OAV_{MAX} correlation for the low

concentration, from the insufficient accuracy of the chemical characterization method (hydrogen sulfide and mercaptans samples correspond to that collected during almost 24h while samples for odor concentration and GC/MS quantification were collected during less than one hour), or from the assumption that mercaptans were mostly methanethiol. Nevertheless, the slope of the fitted line lies is very close to that of the confidence intervals with Log (OAV_{MAX})= 0.98Log (OC). Furthermore, the coefficient of determination (R^2=0.90) denoted a strong linear association between Log (OAV_{MAX}) and Log (OC), suggesting that Log (OAV_{MAX}) could be a good predictor of Log (OC).

Fig. 1

Predicted Log (OAV_{MAX}) as function of measured Log (OC); OAV_{MAX} is the odor activity value (OAV) of the most odorous compound, namely the compound with the highest concentration/ODT value; OC was measured by olfatometry. Hollow points stand outside the confidence interval of OC.

Fig. 2 gives Log (OAV_{SUM}) values as function of Log(OC). As for Log(OAV_{MAX}), Log(OAV_{SUM}) fell outside the Log(OC) confidence interval mostly for mixtures where methanethiol was the most odorous compound and especially when at low and high concentrations, namely when OAV_{MAX} was under 8 x 10^3 and over 6 x 10^4. As for Log (OAV_{MAX}), the slope of the fitted line was very close to that of the confidence interval, where Log (OAV_{SUM}) = 1*Log(OC), namely Log(OAV_{SUM}) = 1.02 Log (OC), with a coefficient of determination R^2=0.87. In conclusion, Log (OAV_{SUM}) can also be an acceptable predictor of Log (OC).

Fig. 2

Predicted Log (OAV_{SUM}) as function of measured Log (OC); OAV_{SUM} was obtained by summing the OAV of every odorous compound found in the gas sample; Odor concentration (OC) was measured by olfatometry. Hollow points are out of the confidence limits of the OC measure.

However to determine odor concentration, on basis of Fig. 1 and 2, OAV_{MAX} showed a higher coefficient of determination than OAV_{SUM}. Although OAV_{MAX} and OAV_{SUM} are functions which are far apart, their linear regression shows a numerically similarity (Log (OAV_{SUM})=1.04Log (OAV_{MAX}) and R^2=0.98; data not show). Consequently, for most of the samples analyzed, the odor activity value (OAV) was mainly displayed by a single compound. In other words, a limited percentage of the odor activity charge is displayed by secondary compounds. Therefore, a quantitative study of OAV_{MAX} and OAV_{SUM} correlation with the odor concentration must be investigated.

3.3. Quantitative evaluation of odor activity

Table 3 gives the numbers of samples where only OAV_{MAX}, only OAV_{SUM} and when both values fell outside the 95% confidence interval of the odor concentration measurement. The mean of the absolute Relative Deviation value is also presented.

Table 3

Comparison of the absolute Relative Deviation of OAV_{MAX} and OAV_{SUM} with respect to the 95% confidence interval for odor concentration measurement

The highest odor activity value in a gas sample (OAV_{MAX}) was within the confidence interval of odor concentration (OC) for 62% gas samples (Fig. 1) whereas the sum of the odor activity values of a gas sample (OAV_{SUM}) for 52% (Fig. 2). For all the OAV_{MAX} and the OAV_{SUM} outside the confidence interval, the mean Relative Deviations (RDs) were of 53 and 73%, respectively. As result, the mean absolute RD value indicated that OAV_{MAX} was, on the average, closer to the corresponding odor concentration interval than OAV_{SUM}. Similarly, when the mixtures showed that both, OAV_{MAX} and OAV_{SUM}, were outside the confident interval of the odor concentration, the Relative Deviation remained lower for OAV_{MAX}, namely at 68% versus 103% for OAV_{SUM}. Finally, the Fig. 3 shows the distributional characteristics of the Relative Deviation when the highest odor activity value (OAV_{MAX}) and the sum of the odor activity values (OAV_{SUM}) from a gas sample were outside the confident interval of the odor concentration measurement.

Fig. 3

Box plot of the Relative Deviation between the closest odor concentration interval boundaries (OC_{INT}) and the maximal odor activity value within a sample outside the odor concentration confident interval, and; between OC_{INT} and the sum of every odor activity values of a sample outside the odor concentration confident interval

The range of Relative Deviation (RD) between the sum of the odor activity values from a gas sample (OAV_{SUM}) and the closest odor concentration interval boundaries (OC_{INT}) was larger than the range of RD between the highest odor activity value from a gas sample (OAV_{MAX}) and OC_{INT} (Fig. 3). The OAV_{SUM} varied from -73 to 300% against -80 to 200% for OAV_{MAX}. Moreover, 50% of the OAV_{MAX} data set was displayed in a relative deviation interval of -33 to 45%, whereas, for OAV_{SUM}, this interval ranged from 22 to 74%. Since the Relative Deviation for OAV_{MAX} was closer to OC_{INT} than that computed for OAV_{SUM}, OAV_{MAX} better predicted the odor concentration (OC) with OAV_{SUM} overestimating OC.

The Relative Deviation between OC and OAV_{MAX} or OAV_{SUM} was very high especially when OC was low, namely under 3×10^3 $OU.m^{-3}$. Even if the statistical analysis of too few samples with such a low odor concentration was not possible, the following were investigated with no resulting conclusion: the influence on odors of some mitigating effects such as NH_3 concentration [2]; the number of sample compounds with a concentration exceeding the odor detection threshold; the distribution of the odor activity value among compounds within the sample, such as OAV_{MAX}/OAV_{MAX2} and as provided in the supplementary material 5), and; the closeness of the odor activity values among compounds (results not shown). Also, the relative deviation was influenced by: the method used for mercaptans analysis; the exclusion of compounds without known odor detection threshold; too high or too low a value for the geometric mean of odor detection threshold; the assumption that odor is linearly correlated to concentration, and; the negligible synergy assumed among odorous compounds.

Limited research work correlates the highest odor activity values for a gas sample to its odor concentration. However, several studies correlated the odor intensity with respect of the VDI 3881 [61], ASTM E544-10 [62]) measured at supra-threshold with the theoretical intensity derived from compound concentration forming synthetic mixtures. Kim and Park [9] showed that odor intensity could be determined by a single predominant compound rather than by the sum or average of all individuals. Kim [63] and Zhao et al. [64] also found that the odor intensity from compound mixtures with similar chemical properties could be mostly characterized by averaging the odor intensity potential of all the contributors. The relevance of the "highest odor activity value compound model" must be cautiously considered as further investigation is necessary.

The literature has generally favoured the correlation between odor concentration (OC) and the sum of the odor activity values for a gas sample (OAV_{SUM}) even if the numerical addition of odor activity value, representing the theoretical dilution factor, does not correspond to the method used in olfactometry. Kim and Park [9] found a strong correlation (Pearson coefficient of 0.866) between OAV_{SUM} and OC, without presenting sufficient data to appreciate the closeness between OAV_{MAX} and OAV_{SUM}. Parker et al. [6] correlated OC to OAV_{SUM}, to find a 2 to 3 fold underestimation of OC. However, the range of measured odor concentrations was quite low, namely from 3×10^1 to 8×10^3 $OU.m^{-3}$. In this range, OAV_{SUM} can be easily underestimated, especially for compounds with a very low odor detection threshold. In this study, supplementary materials 4 lists all cases with compounds detected below their detection limits. Moreover, supplementary materials 4 presents the maximum odor activity value underestimation, defined as the ratio of the method detection

557 limits by the odor detection threshold of the considered compound for each compounds and
558 the sum of the odor activity value of a gas sample.
559
560 3.4. Emissions profiles of odor concentration and the main odorous compounds
561 Fig. 4a, 4b and 4c compares Log (OAV) and Log (OC) for the leading odorous
562 compounds of the gas sample collected during the composting processes applied. As
563 previously mentioned, the similarity between a sample's odor concentratin (OC) and its
564 highest odor activity value (OAV_{MAX}) or the sum of its odor activity values (OAV_{SUM})
565 required a cautious interpretation because of the "log-log correlation". Nevertheless, the
566 Log (OAV_{MAX}) profile emissions (hollow points) better described Log (OC) variations. For
567 the first 4.6 days, OAV_{MAX} was much lower than OC and methanethiol was the most
568 odorant compound. Thereafter, OAV_{MAX} followed, as expected, the same trend as OC and
569 was relatively close, confirming that OAV_{MAX} is a good predictor of OC. Then, hydrogen
570 sulfide was found as the most odorous compound except for the samples on day 15 with a
571 peak of trimethylamine, whatever the process conditions. The odor emissions decreased
572 significantly after 15 to 20 days at which time no leading odorous compound could be
573 clearly identified.
574 Accordingly, mercaptans were emitted when the need for O_2 was highest and when the
575 redox potential was the lowest whereas hydrogen sulfide was emitted at a slightly lower
576 redox potential. Finally, the second and the third material turning operation, on days 22 and
577 29, influenced neither OAV_{MAX} nor OC (Fig. 4a, 4b and 4c) emissions while an increase in
578 O_2 consumption and temperature indicated that biodegradation was still in progress. Thus,

579 the easily biodegradable fraction of organic matter, responsible for the highest O_2 demand,
580 seemed to produce conditions for the emission of the most odorous compounds.
581 The distribution of the odor activity value within a sample also indicates the
582 perspectives for odor abatement, with the removal of the most odorous compounds not
583 necessarily generating a strong odor decrease. The extent of the odor decrease will depend
584 of the next highest odor activity value perceptible during odor concentration measurement.
585 Consequently odor treatment must target in decreasing order, the compounds showing the
586 highest odor activity value. Thus, the number of compounds to be targeted for odor
587 abatement can vary greatly.
588
589 **Fig. 3**
590 Composting emissions profiles of odor concentration (OC) and odor activity value (OAV)
591 for the leading odorous compounds, namely methanethiol (CH_3SH), trimethylamine (TMA)
592 and hydrogen sulfodoride (H_2S). Full points indicate that the highest odor activity value is
593 produced by TMA, H_2S or CH_3SH.
594
595 The Fig. 5a, 5b, 5c and 5d give the log (OAV) profiles of the leading odorous
596 compounds and the log (OC) measured during the various storage processes. Methanethiol
597 always produced the highest odor activity value from gas samples likely because of the low
598 redox potential created by the storage conditions. Slight discrepancies were found between
599 odor concentration and the highest odor activity value when storing fresh PSS and fresh
600 PSS mixed with BA, as high concentrations of mercaptan were produced (Fig. 5a and 5b).
601 In contrast, the 15 and 30 days composts were responsible for lower mercaptan

602 concentrations and, even with similar trends, a larger discrepancy between odor
603 concentration and the highest odor activity values. A more accurate identification of the
604 mercaptans would likely improve this correlation.
605
606 **Fig. 4**
607 Emissions profiles of odor concentration (OC) and odor activity values (OAV) for the
608 leading odorous compounds, namely methanethiol (CH_3SH), trimethylamine (TMA) and
609 hydrogen sulfide (H_2S), emitted during the storage of fresh pig slaughterhouse sludge
610 (PSS), fresh pig slaughterhouse sludge mixed with bulking agent (PSS+BA) and composted
611 pig slaughterhouse sludge after 15 and 30 days of treatment. Full points indicate that the
612 highest odor activity value is produced by TMA, or H_2S or CH_3SH.
613
614 **4. Conclusion**
615
616 The objective of this research was to correlate the chemical characterization of odor
617 emissions with their odor concentration as measured by olfactometry. The emissions
618 analysed in this project were obtained from the composting and storage of pig
619 slaughterhouse sludge. Two correlations were investigated to relate odor concentration
620 (OC) with the chemical composition of the gas sample. The first, based on principles of
621 olfactometric analysis, assumed that the highest odor activity value of the gas sample
622 (OAV_{MAX}) corresponded to OC, whereas the second used the sum of the odor activity
623 values for each compound in the sample.

624 The value of the highest OAV quantitatively gave a better prediction of the odor
625 activity value, as compared to that of the sum of OAVs. However, OAV_{MAX} and OAV_{SUM}
626 were two close mathematical functions, as both showed a good linear regression with the
627 odor concentration, indicating that both could predict the odor concentration. A qualitative
628 comparison of OAV_{MAX} and OAV_{SUM} indicated that OAV_{MAX} was a more relevant
629 predictor than OAV_{SUM} which tended to overestimate the odor concentration.
630 Three main odorous compounds were found to produce OAV_{MAX} in the 66 samples
631 analyzed: trimethylamine, hydrogen sulfide and mercaptans. Accordingly, the odor
632 determination by dilution-to-threshold method was mostly characterized by the compound
633 with the highest odor activity value (OAV_{MAX}). Nevertheless, OAV_{MAX} did not always fall
634 within the 95% confidence interval established for the odor concentration, because:
635 mercaptans were mostly represented by methanethiol; the quantification method for
636 hydrogen sulfide and mercaptans was not sufficiently accurate; no synergy was presumed
637 between compounds forming the gas samples, and; odor threshold determination was drawn
638 on geometric means to describe the central tendency of the threshold value. Regardless of
639 the mathematical function used for correlation, odor activity values were a poor predictor
640 for low odor concentrations, namely under 1000 $OU.m^{-3}$, likely because very low odor
641 detection threshold are often below the GC-MS detection limits leading to an
642 underestimation of the odor activity value.
643

644 **Acknowledgements**

645 The authors wish to acknowledge La Région Bretagne and l'Université Européenne de
646 Bretagne for their financial contributions and that of the Natural Science and Engineering

Research Council of Canada. We would also like to thank the panelists for their investment and their cooperation during the odor measurements.

References

[1] M. Aatamila, P.K. Verkasalo, M.J. Korhonen, A.L. Suominen, M.R. Hirvonen, M.K. Viluksela, A. Nevalainen, Odor annoyance and physical symptoms among residents living near waste treatment centres, Environmental Research 111 (1) (2010) 164-170.

[2] C.J. Tsai, M.L. Chen, A.D. Ye, M.S. Chou, S.H. Shen, I.F. Mao, The relationship of odor concentration and the critical components emitted from food waste composting plants, Atmospheric Environment 42 (35) (2008) 8246-8251.

[3] C. Coker, Managing odors in organics recycling, BioCycle 53 (4) (2012) 25-28.

[4] M. Schlegelmilch, J. Streese, W. Biedermann, T. Herold, R. Stegmann, Odor control at biowaste composting facilities, Waste Management 25(9) (2005) 917-927.

[5] K.R. Murphy, G. Parcsi, R.M. Stuetz, Non-methane volatile organic compounds predict odor emitted from five tunnel ventilated broiler sheds, Chemosphere 95 (2014) 423 – 432.

669 [6] D.B. Parker, J.A. Koziel, L. Cai, L.D. Jacobson, N. Akdeniz, S.D. Bereznicki, T.T.
670 Lim, E.A. Caraway, S. Zhang, S.J. Hoff, A.J. Heber, K.Y. Heathcote, B.P. Hetchler,
671 Odor and odorous chemical emissions from animal buildings: Part 6. Odor activity
672 value, Transactions of the ASABE. 55(6) (2012) 2357-2368.
673
674 [7] J.E. Friedrich and T. E. Acree, Gas chromatograph olfactometry (GC/O) of dairy
675 products, International Dairy Journal 8(3) (1998) 235-241.
676
677 [8] S.L. Trabue, J.C. Anhalt, J.A. Zahn, Bias of Tedlar bags in the measurement of
678 agricultural odorants, Journal of Environmental Quality 35(5) (2006) 1668-1677.
679
680 [9] K.H. Kim and S.Y. Park, A comparative analysis of malodor samples between direct
681 (olfactometry) and indirect (instrumental) methods, Atmospheric Environment 42(20)
682 (2008) 5061–5070.
683
684 [10] D.B. Parker, Z.L. Perschbacher-Buser, N. A. Cole, J. A. Koziel, Recovery of
685 agricultural odors and odorous compounds from polyvinyl fluoride film bags, Sensors
686 10(9) (2010) 8536-8552.
687
688 [11] E, Gallego. F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Characterization and
689 determination of the odorous charge in the indoor air of a waste treatment facility
690 through the evaluation of volatile organic compounds (VOCs) using TD–GC-MS,
691 Waste Management 32(12) (2012) 2469-2481.

[12] EN 13725, Air Quality – Determination of odor concentration by dynamic olfactometry, AFNOR, 2003.

[13] R. Noble, P.J. Hobbs, A. Dobrovin-Pennington, T.H. Misselbrook, A. Mead, Olfactory response to mushroom composting emissions as a function of chemical concentration, Journal of Environmental Quality 30(3) (2001) 760-767.

[14] D. Hanajima, K. Kuroda, K. Morishita, J. Fujita, K. Maeda, K. Morioka, Key odor components responsible for the impact on olfactory sense during swine feces composting, Bioresource Technology 101(7) (2010) 2306-2310.

[15] I.F. Mao, C.J. Tsai, S.H. Shen, T.F. Lin, W.K. Chen, M.L. Chen, Critical components of odors in evaluating the performance of food waste composting plants. Science of the Total Environment 370(2-3) (2006) 323-329.

[16] N. Defoer, I. De Bo, H. Van Langenhove, J. Dewulf, T. Van Elst, Gas chromatography-mass spectrometry as a tool for estimating odor concentrations of biofilter effluents at aerobic composting and rendering plants, Journal of Chromatography 970(1-2) (2002) 259-273.

713 [17] A.K. Gralapp, W.J. Powers, D.S. Bundy, D.S., 2001. Comparison of olfactometry, gas
714 chromatography, and electronic nose technology for measurement of indoor air from
715 swine facilities. Swine Research Report, 2000. Paper 28 (2001).
716
717 [18] M.J. Hansen, A.P.S. Adamsen, P. Pedersen, A. Feilberg, A., 2012. Prediction of odor
718 from pig production based on chemical odorants. Journal of Environmental Quality
719 41(2012) 436–443.
720
721 [19] V. Blanes-Vidal, M.N. Hansen, A.P.S. Adamsen, A. Feilberg, S.O. Petersen, B.B.
722 Jensen. Characterization of odor released during handling of swine slurry: Part I.
723 Relationship between odorants and perceived odor concentrations. Atmospheric
724 Environment 43(2009) 2997–3005.
725
726 [20] P.J. Hobbs, T.H. Misselbrook, T.R. Cumby. Production and emission of odors and
727 gases from ageing pig waste. Journal of Agricultural Engineering Research 72 (1999)
728 291–298.
729
730 [21] W. Groves and E. Zellers, Investigation of organic vapor losses to condensed water
731 vapor in Tedlar bags used for exhaled-breath sampling, American Industrial Hygiene
732 Association Journal 57 (1996) 257–263.
733
734 [22] J.A. Koziel, J.P. Spinhirne, J.D. Lloyd, D.B. Parker, D.W. Wright, F.W. Kuhrt.
735 Evaluation of sample recovery of malodorous livestock gases from air sampling bags,

736 solid-phase microextraction fi bers, Tenax TA sorbent tubes, and sampling canisters.
737 Journal of the Air and Waste Management Association, 55 (2005) 1147–1157.
738
739 [23] M. Sulyok, M., C. Haberhauer-Troyer, E. Rosenberg, M. Grasserbauer. Investigation
740 of the storage stability of selected volatile sulfur compounds in different sampling
741 containers. Journal of Chromatography A, 917 (2001) 367–374.
742
743 [24] S.L. Trabue, J.C. Anhalt, J.A. Zahn. 2006. Bias of Tedlar bags in the measurement of
744 agricultural odorants. Journal of Environmental Quality 35 (2006) 1668–1677.
745
746 [25] J.M. Guillot and S. Beghi. Permeability to water vapour and hydrogen sulphide of
747 some sampling bags recommended by EN 13725. Chemical Engineering Transaction,
748 15 (2008) 79–85.
749
750 [26] M.J. Hansen, A.P.S. Adamsen, A. Feilberg, K.E.N. Jonassen. Stability of odorants
751 from pig production in sampling bags for olfactometry. Journal of Environmental
752 Quality, 40 (2011) 1096-1102.
753
754 [27] P. Mochalski, B. Wzorek, I. Sliwka, A. Amann. Suitability of different polymer bags
755 for storage of volatile sulphur compounds relevant to breath analysis. Journal of
756 Chromatography B, 877 (2009) 189-196.
757

758 [28] A.Ph. Van Harreveld. Odor concentration decay and stability in gas sampling bags.
759 Journal of the Air and Waste Management Association, 53 (2003) 51–60.
760
761 [29] W. Wardencki. Sulfur compounds: gas chromatography. I.D. Wilson (Ed.),
762 Encyclopedia of separation science, Academic Press, Oxford (2000), 4285–4301.
763
764 [30] M.J. Hansen, A. Feilberg, A.P.S. Adamsen.. Stability of volatile reduced sulphur
765 compounds in the dilution system of an olfactometer. Chemical Engineering
766 Transaction 23 (2010) 67–72.
767
768 [31] M.J. Hansen, A.P.S. Adamsen, A. Feilberg. Recovery of Odorants from an
769 Olfactometer Measured by Proton-Transfer-Reaction Mass Spectrometry. Sensors
770 13(2013) 7860-7871.
771
772 [32] NF T90-015-1, Water quality-Determination of ammonium-Part 1: Titrimetric method
773 after steam distillation, 2000.
774
775 [33] A. Ribes, G. Carrera, E. Gallego, X. Roca, M.J. Berenguer, X. Guardino, Development
776 and validation of a method for air-quality and nuisance odors monitoring of volatile
777 organic compounds using multi-sorbent adsorption and gas chromatography/mass
778 spectrometry thermal desorption system, Journal of Chromatography 1140(1-2) (2007)
779 44-55.
780

781 [34] V. Blazy, A. de Guardia, J.C. Benoist, M. Daumoin, M. Lemasle, D. Wolbert, S.
782 Barrington, Odorous gaseous emissions as influence of process condition for the forced
783 aeration composting of pig slaughterhouse sludge, Waste Management 34(7) (2014)
784 1125-1138.
785
786 [36] L.J. Van Gemert, Odor Threshold – Compilation of Odor Threshold Values in Air,
787 Water and Other Media, Oliemans Punter & Partners BV, 2011.
788
789 [37] Y. Nagata, Measurement of odor threshold by triangle odor bag method, Bulletin of
790 Japan Environmental Sanitation Center 17 (2003) 77–89.
791
792 [38] P.H. Dalton, D.D. Dilks, M.I. Banton, Evaluation of odor and sensory irritation
793 thresholds for methyl isobutyl ketone in humans. American Industrial Hygiene
794 Association Journal 61(2000) 340–350.
795 [39] K. Korneev, E. Yu, Effect of the combined presence of low concentrations of phenol
796 and acetophenone in the urban atmosphere, Hygiene and Sanitation USSR 30 (7–9)
797 (1965) 336–345.
798
799 [40] R. Savenhed, H. Boren, A. Grimvall, Stripping analysis and chromatographic sniffing
800 for the source identification of odorous compounds in driking water, Journal of
801 Chromatography 328 (1985) 219–231.
802

[41] N.B. Imasheva, The substantiation of the maximum permissible concentration of acetophenon in the atmospheric air (in Russia), Hygiene and Sanitation 28 (2) (1963) 3–8.

[42] N.Z. Tkach, Combined effect of acetone and acetophenone in the atmosphere, Hygiene and Sanitation, USSR 30 (7–9) (1965) 179–185.

[43] M.A.M. Smeets, P.J. Bulsing, S. Van Rooden, R. Steinman, J.A. De Ru, N.W.M. Ogink, C. Van Triel, P.H. Dalton, Odor and irritation thresholds for ammonia: a comparison between static and dynamic olfactometry, Chemical Senses 32 (2007) 11-20.

[44] J. Greenman, J. Duffield, P. Spencer, M. Rosenberg, D. Corry, S. Saad, P. Lenton, G. Majerus, S. Nachnani, M. El-Maaytah, Study on the organoleptic intensity scale for measuring malodor, Journal of Dental Research 83 (2004) 81–85.

[45] ADEME, Pollution olfactives, Dunod ed., l'usine nouvelle, Paris, 2005.

[46] H. Ueno, S. Amano, B. Merecka, J. Kosmider, Difference in the odor concentration measured by the trianble odor bag method and dynamic olfactometry, Water Science Technology 59 (2009) 1339–1342.

825 [47] M.A. McGinley, C.M. McGinley, Comparison of field olfactometers in a controlled
826 chamber using hydrogen sulphide as the test odorant, Water Science Technology 50 (4)
827 (2004) 75–82.
828
829 [48] W.S. Cain, M.L. Dourson, M.J. Kohrman-Vincent, B.C. Allen, Human chemosensory
830 perception of methyl isothiocyanate: chemesthesis and odor, Regulatory Toxicology
831 and Pharmacology 58 (2010) 173–180.
832
833 [49] D.S. Yang, R.L. Shewfelt, K.S. Lee, S.J. Kays, Comparison of odor-active compounds
834 from six distincly different rice flavor types, Journal of Agricultural and Food
835 Chemistry 56 (2008) 2780–2787.
836
837 [50] G.Z. Nagy, The odor impact model, Journal of the Air & Waste Management
838 Association, 41 (1991) 1360–1362.
839
840 [51] J.A. Don., Odor measurement and control, Paper presented at odor control in industry,
841 London, March 18 1986.
842
843 [52] Y. Hoshika, T. Imamura, G. Muto, L.J. Van Gemert, J.A. Don, J.I. Walpot,
844 International comparison of odor threshold values of several odorants in Japan and in
845 the Netherlands, Environmental Resources 61 (1993) 78–83.
846

847 [53] J.E. Cometto-Muniz, M.H. Abraham, Olfactory detedtability of homologous
848 nalkylbenzenes as reflected by concentration-detection functions in humans,
849 Neuroscience 161 (2009) 236–248.
850
851 [54] R.H. Gundlach, G. Kenway, A method for the determination of olfactory thresholds in
852 humans, Journal of Experimental Psychology 24(2) (1939) 192-201.
853
854 [55] S.H. Katz and E.J. Talbert, Intensities of odors an irritating effects of warning agents
855 for inflammable and poisonous gases. U.S. Bureau of Mines, Technical report n°480,
856 1930.
857
858 [56] P.M. Wise, T. Miyazawa, M. Gallagher, G. Petri, Human odor detection of
859 homologous carboxylic acids and their binary mixtures, Chemical Senses, 32 (2007),
860 475–482.
861
862 [57] T. Miyazawa, M. Gallagher, G. Petri, P.M. Wise, Odor detection of mixtures of
863 homologous carboxylic acids and coffee aroma compounds by humans, Journal of
864 Agricultural and Food Chemistry (2009) 9895–9901.
865
866 [58] J.E. Cometto-Muniz, M.H. Abraham, Structure-activity relationships on the odor
867 detectability of homologous carboxylic acids by humans, Experimental Brain
868 Research 207 (2010) 75–84.
869

870 [59] G. Parcsi, E.C. Sivret, X. Wang, R.M. Stuetz. Fate of sulfur odorants in odor
871 collection. AWA Odor Specialty Conference 24–25 August, Sydney, 2010.
872
873 [60] J.A. Zahn, A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooper, J.L. Hatfield,
874 Correlation of human olfactory responses to airborne concentrations of malodorous
875 volatile organic compounds emitted from swine effluent, Journal of Environmental
876 Quality 30(2) (2001) 624-634.
877 [61] VDI 3882 Part 1, 1992. Olfactometry Determination of Odor Intensity, Technische
878 Regel. Von Braun, J., 1927. Geruch und molekulare asymetrie, IV. Mitteilung: Die drei
879 1.3-Dimethylcyclohexanone-5 und die vier 1.3-Dimethyl-cyclohexanole-5. Berichte der
880 deutschen chemischen Gesellschatt (A and B Series),60(11), 1927, 2438-2446.
881
882 [62] ASTM standard E544-10, Standard practices for referencing suprathreshold odor
883 intensity, ASTM international (2010), West Conshohocken, PA.
884
885 [63] K.H. Kim, The averaging effect of odorant mixing as determined by air dilution
886 sensory tests: A case study on reduced sulfur compounds, Sensors 11 (2011) 1405-
887 1417.
888
889 [64] P. Zhao, J.M. Liu, S.C. Tang, The interaction of mixing odorants with similar
890 chemical properties: A case study on ketone compounds (Conference paper),
891 Advanced Materials Research, International Forum on Materials Analysis and Testing
892 Technology 850-851 (2013) 32-37.

893 [65] V. Blazy, A. de Guardia, J.C. Benoist, M. Daumoin, M. Lemasle, D. Wolbert, S.
894 Barrington, Process Conditions Influence on Pig Slaughter House Compost Quality
895 Under Forced Aeration, Waste and Biomass Valorization 5(3) (2014) 451-468.

Table 1

Mixtures compositions and experimental conditions

	Storage experiments				Composting experiments		
Material composition	**Fresh PSS**	**Fresh PSS+BA**	**PSS compost at 15 days**	**PSS compost at 30 days**	**Fresh PSS**		
PSS or compost fresh mass (kg)	24.44	11.57	10.75	11.07	59.76	58.52	58.75
Bulking agent fresh mass (kg)	-	9.63	-	-	43.75	42.84	32.25
Water added (kg)	-	-	-	-	-	6.83	-
Fresh mass ratio (BA/PSS)	-	0.83	-	-	0.73	0.73	0.55
Mixture moisture (%)	76.3	51.9	46.1	35.6	61.2	63.7	63.6
Experimental conditions							
Mean aeration rate ($L.h^{-1}$)	42.2	38.4	42.5	41.7	553	554	556
number of turning material	-	-	-	-	3	3	3
end of the experimentation (days)	29.6	13.9	15.7	15.9	35.5	35.5	35.5

PSS: pig slaughterhouse sludge; BA: bulking agent

Table 2

Gaseous compounds identified from emissions collected during the composting and the storage of pig slaughterhouse sludge

Compounds	CAS number	Quantification ion (m/z)	Calibration coefficient	ODT ($mg.m^{-3}$)	MDL_{MAX} /ODT	ODT References
Ketones						
2 Butanone	78-93-3	43	680	22.7	-	Nagata [37]
2 Butanone-3- methyl	563-80-4	72	645	1.8	-	Nagata [37]
2 Butanone 3,3 dimethyl	75-97-8	43	1000†	0.176	-	Nagata [37]
2 Hexanone	591-78-6	58	1000†	0.098	-	Nagata [37]
2-Pentanone	107-87-9	86	680	0.098	-	Nagata [37]
2-Pentanone-3-methyl	565-61-7	43	977	0.098	-	Nagata [37]
3 Pentanone 2methyl	565-69-5	43	1000†	N-D	-	-
Acetone	67-64-1	58	500	101	-	Nagata [37]. Dalton et al. [38]
Acetophenone*	98-86-2	105	71	0.0175	4.6	Korneev [39]; Savenhed et al. [40]; Imasheva [41]; Tkach [42]
N-compounds						
Ammonia	7664-41-7	-	-	1.45	-	Nagata [37] ; Smeet et al. [43]
Methenamine	100-97-0	140	1000†	N-D	-	-
Trimethylamine*	75-50-3	58	775	0.00006	1333	Nagata [37]; Greenman et al. [44]
S-compounds						
Dimethyl disulfide*	624-92-0	94	1068	0.0085	9	Nagata [37]
Dimethyl sulfide*	75-18-3	62	915	0.0076	11	Nagata [37]
Dimethyl trisulfide*	3658-80-8	126	301	0.0087	9	ADEME [45]
Methanethiol	74-93-1	-	-	0.00031	-	Nagata [37], Greenman et al. [44]
Hydrogen sulfide	7783-06-4	-	-	0.00053	-	Nagata [37]; Ueno et al. [46]. McGinley and McGinley [47]
Alcohols						
1-Butanol	71-36-3	56	1240	0.45	-	Ueno et al. [46] ; Cain et al. [48]
1-Butanol- 3- methyl	123-51-3	56	1000†	0.01	8	Nagata [37]
1-Pentanol	71-41-0	31	1400	0.256	-	Nagata [37] ; Yang et al. [49]
1-Propanol	71-23-8	56	1000†	0.24	-	Nagata [37]
1-Propanol-2-methyl	78-83-1	43	1000†	0.033	2	Nagata [37]
2-Butanol	78-92-2	45	1000†	0.66	-	Nagata [37]
Ehtyl hexanol	104-76-7	57	1000†	0.8	-	Nagy et al. [50]
Ethyl alcohol	64-17-5	31	1000†	0.99	-	Nagata [37]
Isopropyl alcohol	67-63-0	45	1000†	65	-	Nagata [37]
Methanol	67-56-1	31	2600	43	-	Nagata [37]
Aromatic hydrocarbons						
Phenol	108-95-2	94	2130	0.035	2	Nagata [37]; Don [51]; Hoshika [52]
Styrene	100-42-5	104	1095	0.149	-	Nagata [37]
Toluene	108-88-3	91	3611	0.38	-	Cometto-Muniz and Abraham [53]
Aliphatic hydrocarbons						
1-3-Pentadiene	504-60-9	67	1405	N-D		
Terpenes						
Alpha-pinene	80-56-8	91	975	0.1	-	Nagata [37]
Camphor	76-22-2	95	1000†	0.49	-	Gundlach and Kenway [54]
Limonene	138-86-3	68	2	0.134	-	Nagata [37]
S and N compounds						
Thiocyanic acid methyl ester	556-64-9	73	416	0.75	-	Katz and Talbert [55]
Acids						
Acid acetic	64-19-7	60	460	0.016	5	Nagata [37], Wise et al. [56], Miyazawa et al. [57]
Propanoic acid	79-09-4	60	1000†	0.017	2	Nagata [37]
Hexanoic acid*	142-62-1	60	1000†	0.0048	17	Cometto-Muniz and Abraham [58]
Aldehyde						
Butanal *	123-72-8	43	1000†	0.0016	25	Nagata [37]; Cometto-Muniz and Abraham [58]

N-D: no data found; ODT: odor detection threshold as referenced from the odor detection threshold database [36];
MDL_{MAX}/ODT indicates how many time the highest GC-MS method detection limit (MDL_{MAX}) exceeded the odor detection threshold (ODT) for a compound;
* Compounds with an ODT lower than the GC-MS method detection limit.
1000†: the coefficient used when the compound was not calibrated.

Table 3

Comparison of the absolute relative deviation of OAV_{MAX} and OAV_{SUM} with respect to the 95% confidence interval for odor concentration measurement

	Number of mixture	Mean Abs RD (%)	
		OAV_{MAX}	OAV_{SUM}
OAV_{MAX} and OAV_{SUM} are outside the confident limits of OC measure	16 (24%)	68	103
OAV_{MAX} is outside the confident limits of OC measure	25 (38%)	53	-
OAV_{SUM} is outside the confident limits of OC measure	31 (47%)	-	73

OC, odor concentration of a gaseous emission measured by olfactometry and corresponding to the number of dilution required for its odor to be undetected; OAV_{MAX} : maximal odor activity value within a mixture ; OAV_{SUM} : sum of every odor activity values of a mixture; Abs RD: absolute relative deviation value

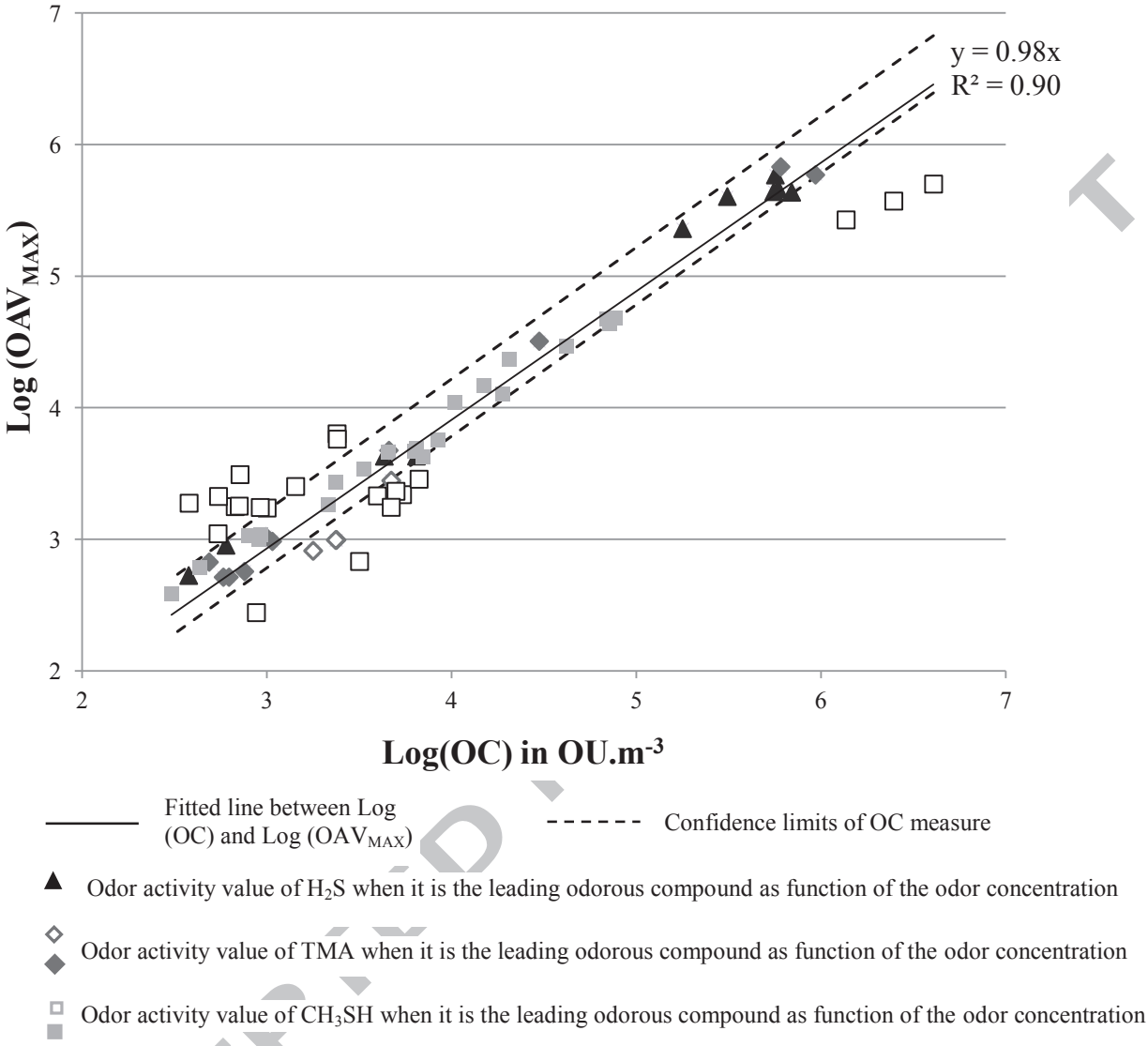


Fig.1 Predicted Log (OAV_{MAX}) as function of measured Log (OC) (OAV_{MAX} is the odor activity value (OAV) of the most odorous compound, namely the compound with the highest concentration/odor detection threshold value; the odor concentration (OC) was measured by olfatometry. Hollow points stand outside the confidence interval of the odor concentration).

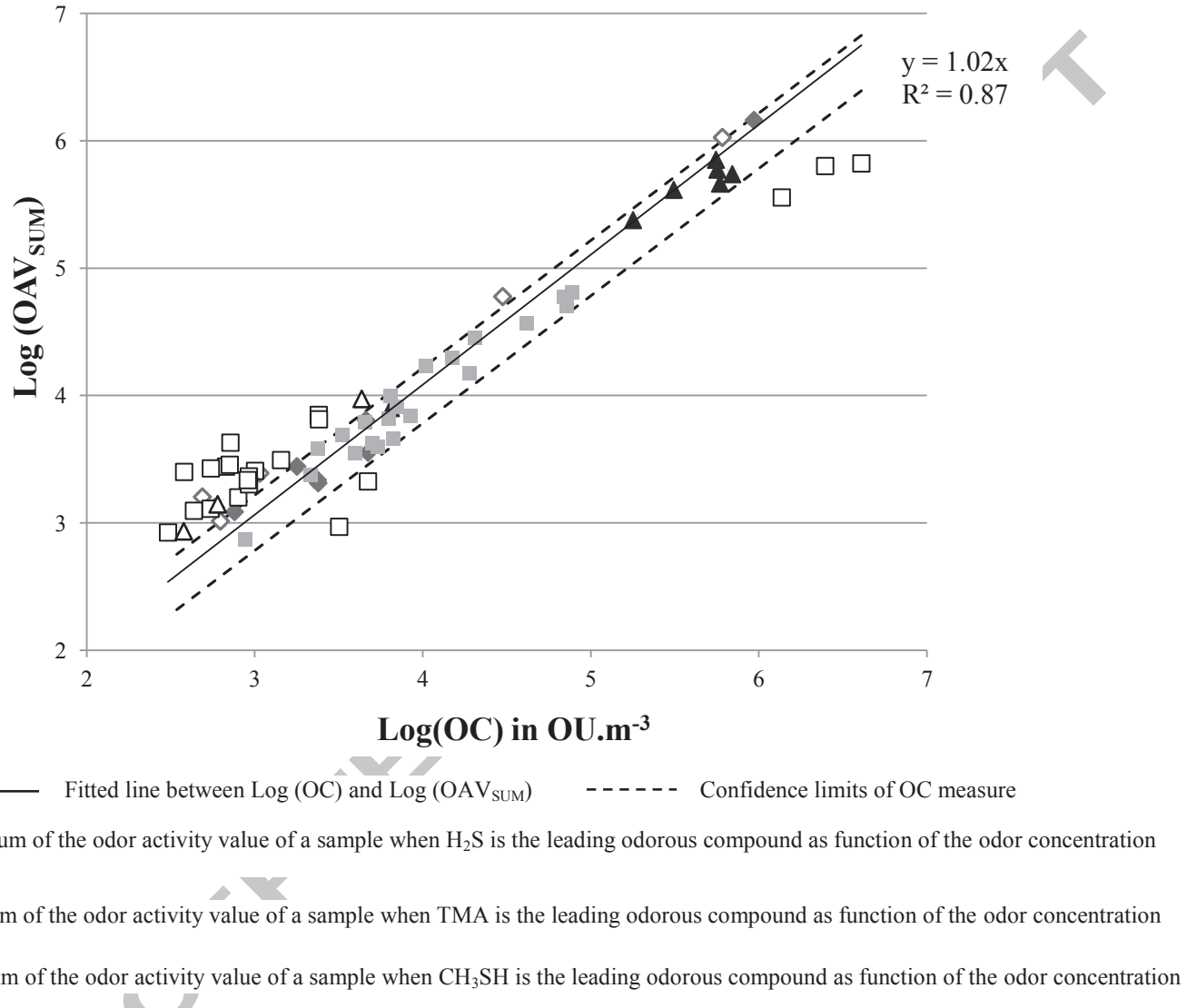
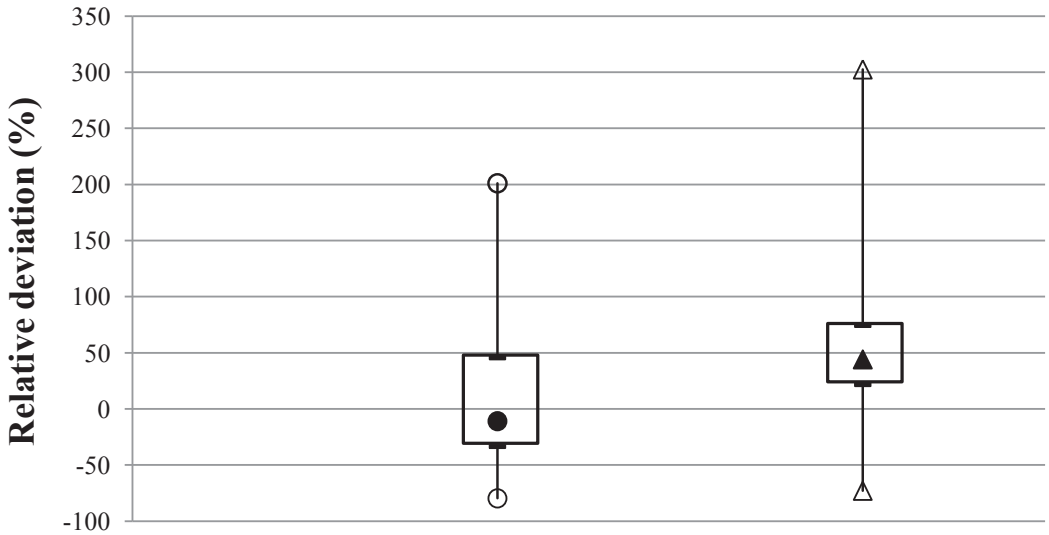


Fig.2. Predicted Log (OAV_{SUM}) as function of measured OC (OAV_{SUM} was obtained by summing the OAV of every odorous compound found in the gas sample; the odor concentration (OC) was measured by olfatometry. Hollow points are out of the confidence limits of the OC measure).



● Box plot of the Relative Deviation between the closest odor concentration interval boundaries and the maximal odor activity value within a sample outside the odor concentration confident interval

▲ Box plot of the Relative Deviation between the closest odor concentration interval boundaries and the sum of every odor activity values of a sample outside the odour concentration confident interval

Fig.3. Box plot of the Relative Deviation between the closest odor concentration interval boundaries (OC_{INT}) and the maximal odor activity value within a sample outside the odor concentration confident interval, and; between OC_{INT} and the sum of every odor activity values of a sample outside the odor concentration confident interval.

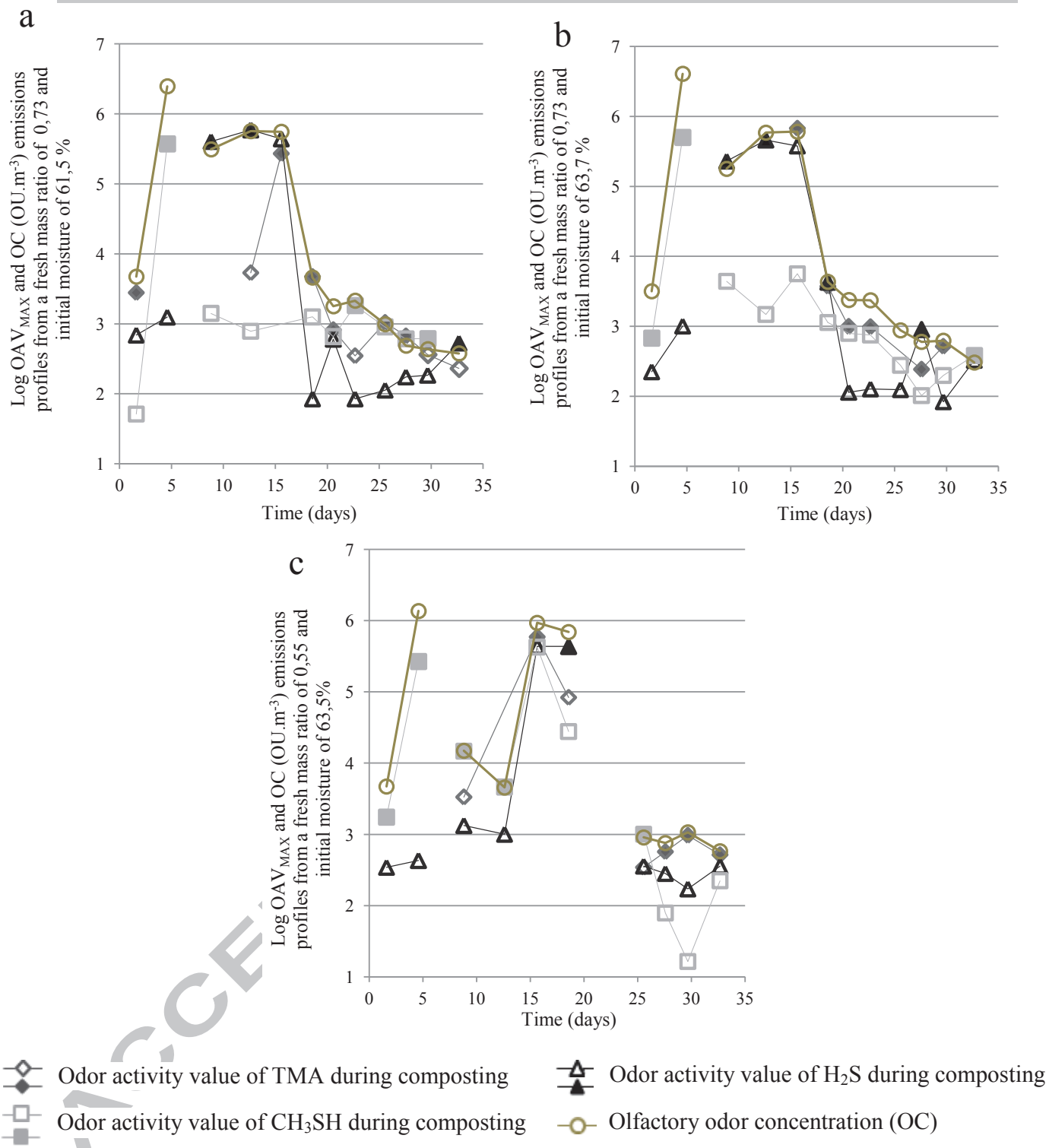


Fig. Composting emissions profiles of odor concentration (OC) and odor activity value (OAV) for the leading odorous compounds, namely methanethiol (CH_3SH), trimethylamine (TMA) and hydrogen sulfide (H_2S). Full points indicate that the highest odor activity value is produced by TMA, H_2S or CH_3SH.

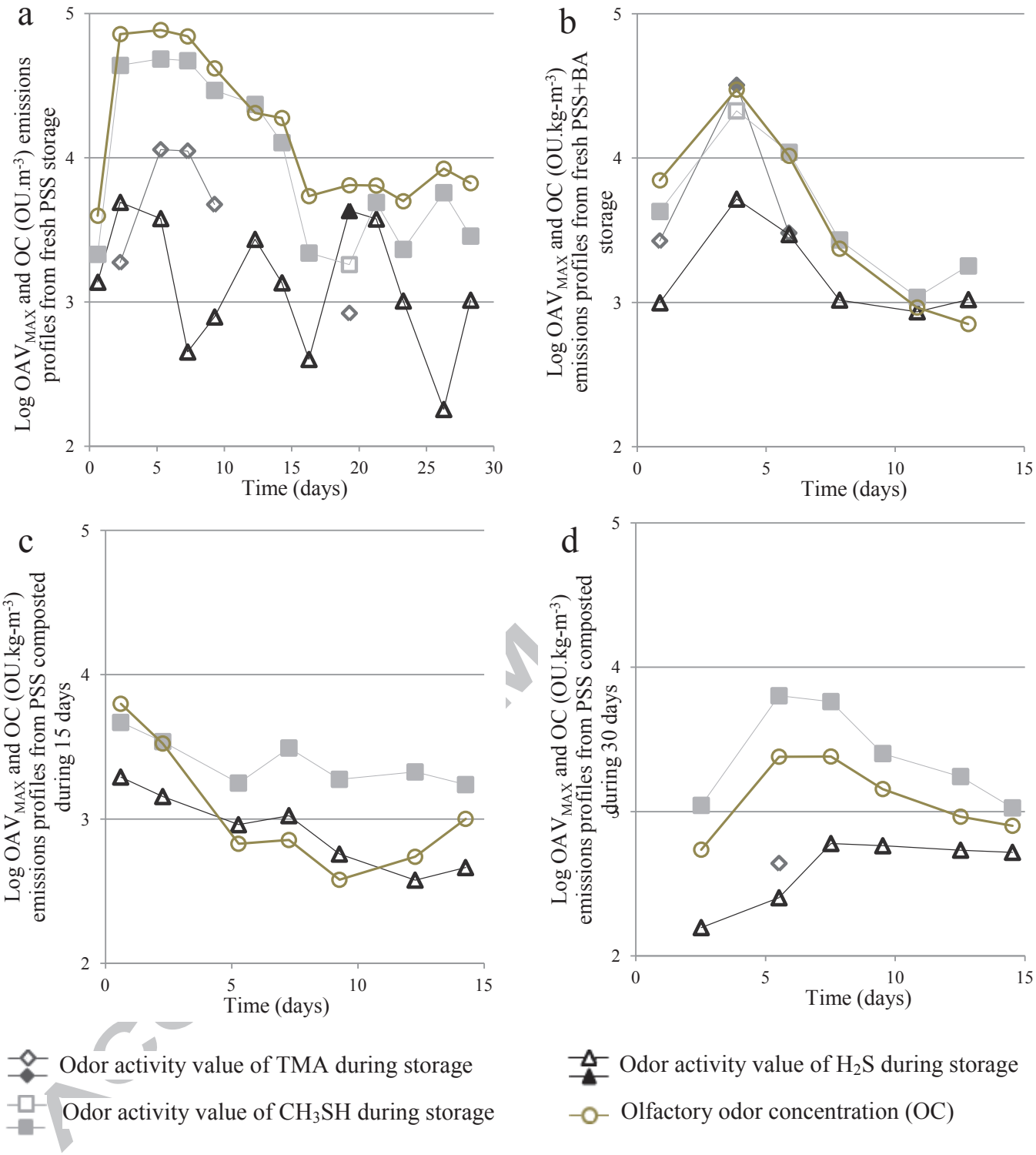


Fig. Emissions profiles of odor concentration (OC) and odor activity values (OAV) for the leading odorous compounds, namely methanethiol (CH_3SH), trimethylamine (TMA) and hydrogen sulfide (H_2S), emitted during the storage of fresh pig slaughterhouse sludge (PSS),

fresh pig slaughterhouse sludge mixed with bulking agent (PSS+BA) and composted pig slaughterhouse sludge after 15 and 30 days of treatment. Full points indicate that the highest odor activity value is produced by TMA, or H_2S or CH_3SH.

□ig□i̇g□□□

PSS composting and storage gas samples were determined by chemical and olfactory analyses

For gas samples, correlations between the chemical composition and its OC was investigated

OAV_{MAX} assumed that OC was equal to the sample's highest OAV value

OAV_{SUM} assumed that OC was equal to the sum of all OAV for sample

The 3 most odorant compound offered a good prediction of the olfactory results.